Synthesis of *N,N′*-dimethyl-*N,N′*-didecyl-3-oxa-diglycolamide for extraction of lanthanides[*]

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A novel extractant, *N,N′*-dimethyl-*N,N′*-didecyl-3-oxa-diglycolamide (DMDDDGA), was designed and synthesized for extraction of lanthanides in the nuclear fuel reprocessing. The extraction behaviors of Gd, Dy, Er and Ho from nitric acid solution were investigated using DMDDDGA in chloroform. The effects of nitric acid concentration, extractant concentration, and temperature on the extraction were investigated. The distribution ratio of lanthanides increases with concentrations of the extractant and nitric acid, but decreases with increasing temperature, which indicates that the extraction process is exothermic. FT-IR spectra indicated that the C=O in DMDDDGA is coordinated with metal ion in the extracted species and the stoichiometries of lanthanides(III) complex are $Gd(NO_3)_3 \cdot 3DMDDDGA$, $Dy(NO_3)_3 \cdot 4DMDDDGA$, $Er(NO_3)_3 \cdot 4DMDDDGA$, and $Ho(NO_3)_3 \cdot 4DMDDDGA$.

Keywords: *N,N′*-dimethyl-*N,N′*-didecyl-3-oxa-diglycolamide, Extraction, Lanthanide, Nitric acid solution

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I. INTRODUCTION

The separation of uranium, thorium and rare earth in reprocessing spent thorium-uranium fuel is an important issue [1]. Lanthanide elements have large thermal neutron capture cross sections, which affect the thermal neutron transmutation of the long lived fission products. So lanthanides must be separated from the high level waste in the Th-U fuel reprocessing. The utilization of diglycolamides in the extraction of actinides, lanthanides, and some other metals has attracted considerable interest [2, 3]. The 3-oxa-diglycolamide extractants with symmetrical substantial groups on N atom, such as *N,N,N′,N′*-tetraoctyl-3-oxa-diglycolamide (TODGA), were studied extensively because of its complete incinerability and desirable coordination properties of oxygen to lanthanide and actinide ions [4–16]. However, the big substituent alkyl group, octyl, connected with N atom shows high steric hindrance, which results in the decrease in the extraction distribution. We investigated synthesis of unsymmetrical amides and the extraction properties for lanthanides [17, 18], and found that *N,N′*-dimethyl-*N,N′*-dioctyl-3-oxa-diglycolamide (DMDODGA) showed higher affinity toward lanthanide ions than TODGA [17] or *N,N,N′,N′*-tetrabutyl-3-oxa-diglycolamide [18] with symmetrical bigger alkyl group resulting in big steric hindrance.

In this paper, we report a new unsymmetrical extractant, *N,N′*-dimethyl-*N,N′*-didecyl-3-oxa-diglycolamide, with longer alkyl group to improve the solubility of the diglycolamide and its adduct in the organic phase and methyl groups to keep the steric hindrance to minimum. DMDDDGA is synthesized by a simple three-step route and the extraction behavior for lanthanides(III) is investigated. The results show that the designed extractant has strong extraction capability

for lanthanides(III).

II. EXPERIMENTAL

A. Reagents and experimental equipment

All chemicals are of reagent grade. Carbon, hydrogen, and nitrogen were analyzed by a Perkin-Elmer PE2400C elemental analyzer. IR spectra were recorded at 4000–$500\,\text{cm}^{-1}$ with KBr discs on a Bio-Rad FTS-165 spectrometer. The ^{1}H was obtained with a Bruker DPX-400 NMR. DMDDDGA was synthesized in the following three steps (Fig. 1).
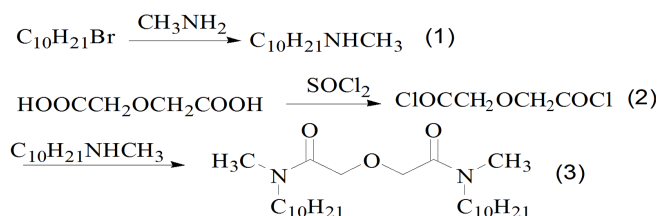

$$C_{10}H_{21}Br \xrightarrow{CH_3NH_2} C_{10}H_{21}NHCH_3 \quad (1)$$

$$HOOCCH_2OCH_2COOH \xrightarrow{SOCl_2} ClOCCH_2OCH_2COCl \quad (2)$$

Fig. 1. Synthesis scheme of DMDDDGA.

1. N-methyl decyl amine

1-Bromodecane (25 mL, 0.12 mol), 175 mL of 30% methylamine alcohol solution were stirred at $110\,^\circ\text{C}$ for 48 h in a 200-mL autoclave. The methylamine alcohol solution was removed by distillation and the residue was distilled (236–$238\,^\circ\text{C}/0.1\,\text{MPa}$) to give 14.36 g *N*-methyl decyl amine, with the yield of 70%. IR (cm^{-1}/film): 3286, 2927, 2853, 2789, 1463 and 724. ^{1}H NMR ($400\,\text{MHz}$, CDCl$_3$): δ 2.479–2.449 (m, 2H, CH$_2$NH), 2.351–2.290 (m, 3H, NHCH$_3$), 1.372 (s, 2H, CH$_2$CH$_2$NH), 1.182 (s, 14H, (CH$_2$)$_7$), 1.087 (s, 1H, NH), 0.802–0.772 (m, 3H, CH$_2$CH$_3$).

2. Diglycoloyl chloride

A mixture of diglycolic acid (34.4 g, 0.26 mol), thionyl chloride (220 mL, 370 g, 3.08 mol), and a few drops of pyridine were stirred at reflux for 5 h. The thionyl chloride was removed by distillation and the residue was distilled to produce diglycoloyl chloride (39 g) as yellow oil (85–88 °C/5 kPa), with the yield of 87% [17].

3. Synthesis of DMDDDGA

N-methyl decyl amine (120 g, 0.7 mol), pyridine (56.5 mL, 0.7 mol) and benzene (200 mL) were mixed and cooled to 5 °C. Then, 34 mL of diglycoloyl chloride (0.28 mol) dissolved in benzene (50 mL) was added dropwise under stirring. The reaction was kept for 2 h in an ice bath and 1 h at ambient temperature. The residue was filtered and the filtrate was washed with 1 mol/dm^3 HCl, 3 mol/dm^3 NaOH, and water, successively. The organic phase was dried over anhydrous Na$_2$SO$_4$. Benzene was removed by distillation and DMDDDGA, and reddish brown oil (183.5 g) was obtained by column chromatography, with the yield of 56%. IR (cm^{-1}/film): 2926, 2855, 1660, 1467, 1399 and 1122. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.273 (d, 4H, CH$_2$OCH$_2$), 3.335–3.183 (m, 4H, NCH$_2$), 2.909 (d, 6H, NCH$_3$), 1.498(s, 4H, NCH$_2$CH$_2$), 1.229(s, 28H, (CH$_2$)$_7$), and 0.862–0.833 (m, 6H, CH$_2$CH$_3$). Elemental analysis C$_{26}$H$_{52}$N$_2$O$_3$ (calculated values are shown in brackets): C 70.87% (70.86%), H 11.20% (11.89%), and N 6.23% (6.36%).

B. Extraction procedure

Equal volumes of aqueous phase and organic phase were agitated for 30 min to obtain equilibrium at a constant temperature. The two phases were centrifuged and assayed by taking known aliquots (0.05–0.10 mL) from the aqueous phase. The M^{3+} content in aqueous phase was determined by Arsenazo-III visible spectrophotometric analysis, and the M^{3+} content in organic phase was obtained by subtracting the aqueous concentrations from the total initial aqueous concentration of M^{3+}. The distribution ratio (*D*) was calculated as the ratio of the concentration of M^{3+} in the organic phase to that in the aqueous phase.

C. FT-IR characterization

Equal volumes of 0.20 mol/dm^3 DMDDDGA solution and 0.05 mol/dm^3 of trivalent lanthanide ions were agitated. FT-IR spectra of the organic phase were recorded using a potassium bromide window with scanning times of 16 and the resolution of 2 cm^{-1}.
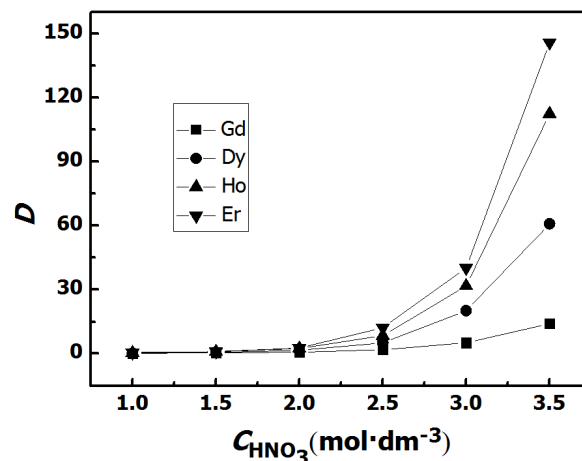

Fig. 2. Effect of HNO$_3$ concentration on extraction of lanthanides. $C_{M^{3+}} = 5.00 \times 10^{-3}$ mol/dm^3, $C_{DMDDDGA} = 0.05$ mol/dm^3, 298 K.

III. RESULTS AND DISCUSSION

A. Effect of HNO$_3$ content on distribution ratio

The extraction of lanthanides(III) from nitric acid medium was studied using DMDDDGA within the initial nitric acid concentration of 1.0–3.5 mol/dm^3 (Fig. 2).

Nitric acid concentration has little effect on the distribution ratio in the range of 1.0–2.0 mol/dm^3. The *D* value increases markedly with the nitric acid concentration above 2.0 mol/dm^3, indicating that the anion NO$_3^-$ plays an important co-ion role in this extraction system. Fig. 2 also shows that the extraction behaviour of DMDDDGA on the Gd(III), Dy(III), Ho(III) and Er(III) is a positive sequence with the atomic number. Shimojo *et al.* [19] also found similar phenomena that the heavier lanthanide cations were effectively extracted.

B. Effect of DMDDDGA content on extraction

The extraction of trivalent lanthanide elements (M^{3+}) from HNO$_3$ solution by DMDDDGA can be expressed as:

$$M^{3+} + 3NO_3^- + nDMDDDGA = M(NO_3)_3 \cdot nDMDDDGA. \quad (1)$$
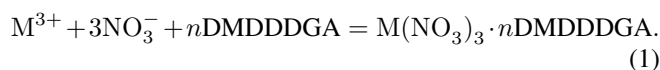
The extraction equilibrium constant is

$$K_{ex} = \frac{a_{M(NO_3)_3 \cdot nDMDDDGA_{(o)}}}{a_{M^{3+}} a_{NO_3^-}^3 a_{DMDDDGA_{(o)}}^n}$$

$$= \frac{[M(NO_3)_3 \cdot nDMDDDGA]_{(o)}}{\gamma_{M^{3+}} \gamma_{NO_3^-}^3 [M^{3+}][NO_3^-]^3 [DMDDDGA]_{(o)}^n}. \quad (2)$$

The conditional equilibrium constant is

$$K = \frac{D}{[NO_3^-]^3 [DMDDDGA]_{(o)}^n}, \quad (3)$$

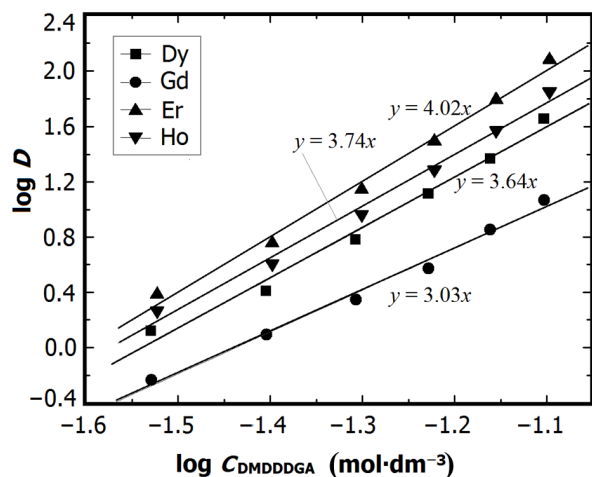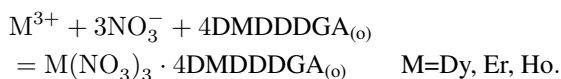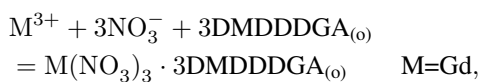Fig. 3. Effect of DMDDDGA concentration on extraction of lanthanides C_{HNO_3} =2.5 mol/dm^3, $C_{M^{3+}}$ =5 × 10^{-3} mol/dm^3, 298 K.

Fig. 4. FT-IR spectra of organic phase loaded Ln(III) with DMDDDGA in chloroform.

where [M^{3+}] is the aqueous concentration of M^{3+}, and [M(NO$_3$)$_3$·nDMDDDGA]$_{(o)}$ is the concentration of extracted species in the organic phase. With a constant [NO$_3^-$], Eq. (3) can be rearranged into Eq. (4) by taking the logarithm:

$$\log D = \log K + n \log [\text{DMDDDGA}]_{(o)} - 3\log[\text{NO}_3^-]. \tag{4}$$

From Eq. (4), n can be estimated from the slope analysis of the relationship between $\log D$ and $\log[\text{DMDDDGA}]_{(o)}$. The effect of DMDDDGA concentration on the distribution ratio of lanthanides is shown in Fig. 3. It can be seen that $\log D$ increases with DMDDDGA concentration, and the slopes are n = 4.02, 3.74, 3.64 and 3.03 for Er^{3+}, Ho^{3+}, Dy^{3+} and Gd^{3+}, respectively. So, the stoichiometries of the main extracted species can be Gd(NO$_3$)$_3$·3DMDDDGA and M(NO$_3$)$_3$·4DMDDDGA (M = Dy^{3+}, Ho^{3+}, Er^{3+}). Similar variations in stoichiometry of the metal ligand complex were corroborated by EXAFS studies [20] of Er^{3+}-DGA complex in ethanol, and it was suggested that only two of the four DGA molecules might be bonded in tridentate fashion with some water molecules in the inner coordination sphere.

The extraction mechanism can be expressed as

$$\text{M}^{3+} + 3\text{NO}_3^- + 3\text{DMDDDGA}_{(o)}$$
$$= \text{M(NO}_3)_3 \cdot 3\text{DMDDDGA}_{(o)} \qquad \text{M=Gd,}$$

$$\text{M}^{3+} + 3\text{NO}_3^- + 4\text{DMDDDGA}_{(o)}$$
$$= \text{M(NO}_3)_3 \cdot 4\text{DMDDDGA}_{(o)} \qquad \text{M=Dy, Er, Ho.}$$

The $\log K$ of extracting Gd^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+} with DMDDDGA in chloroform from nitric acid calculated using Eq. (3) were 3.10 ± 0.06, 4.84 ± 0.06, 5.03 ± 0.06 and 5.21 ± 0.07, respectively. The asymmetric DMDDDGA has a better extraction effect than TBDGA in our previous work [21].

FT-IR spectra of the organic phase loading extracted species were recorded (Fig.4). The wave number of the stretching freq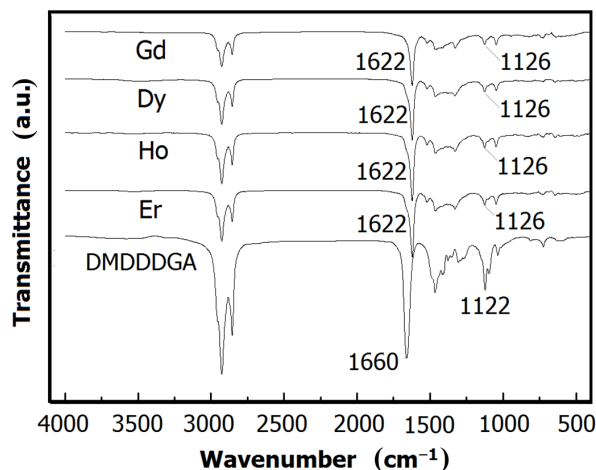uency of C=O band is shifted from 1660 to 1622 cm^{-1}. Sasaki *et al.* [22] also reported that the wave number of C=O is shifted to lower number after extraction. The FT-IR results indicated that the carbonyl groups of DMDDDGA molecules are coordinated to metal ions. The wave number of C−O−C is shifted from 1122 cm^{-1} to 1126 cm^{-1}. The structural characterization of lanthanum(III) complex coordinated by diglycolamide (DGA) ligands shows that the ligand is tridentated [23].
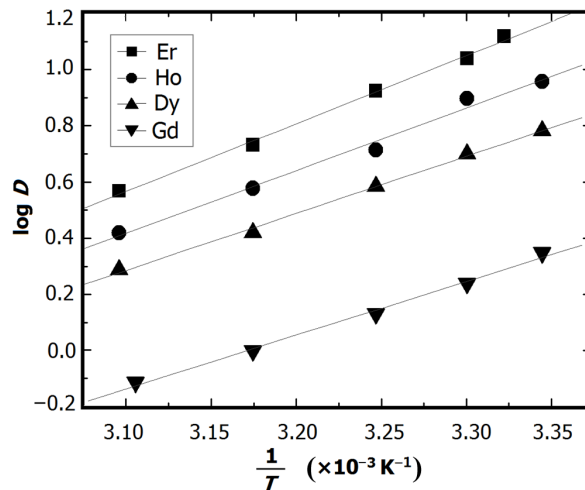

Fig. 5. $\log D$ vs. $1/T$ for extraction of lanthanides(III) with DMDDDGA. $C_{M^{3+}}$ =5 × 10^{-3} mol/dm^3, C_{HNO_3} =2.5 mol/dm^3, $C_{DMDDDGA}$ =0.05 mol/dm^3.

C. Temperature effect on extraction

Figure 5 shows the temperature effect on the extraction distribution ratio. The extraction rate decreases with increasing temperature. From the Van't Hoff equations [24], the thermo-

dynamic parameters can be calculated by [24]:

$$\log D = -\Delta H/(2.303RT) + \text{C}, \tag{5}$$

where, R is the gas constant and C is a conditional constant. So, $-\Delta H/(2.303R)$ is the slopes in Fig. 5. From Eq. (5) and Fig. 5, we have $\Delta H = -36.57$ kJ/mol, -38.87 kJ/mol, -42.70 kJ/mol and -46.34 kJ/mol for Gd^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+}, respectively, which indicates that the extraction reactions are exothermic.

IV. CONCLUSION

The novel unsymmetrical extractant, DMDDDGA, has been successfully synthesized by a simple three-step route. DMDDDGA shows high affinity for lanthanides and good extraction capability from nitric acid solutions. The extraction distribution increases sharply with HNO_3 concentration above 2 mol/dm³, and with the DMDDDGA concentration. The extraction complex are $Gd(NO_3)_3 \cdot 3DMDDDGA$ and $M(NO_3)_3 \cdot 4DMDDDGA$ ($M = Dy^{3+}$, Ho^{3+} and Er^{3+}). Temperature has a significant effect on the lanthanides(III) extraction. The extraction process is exothermic with the reaction enthalpy of -36.57 kJ/mol, -38.87 kJ/mol, -42.70 kJ/mol and -46.34 kJ/mol for Gd^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+}, respectively. FT-IR spectra indicate that the carbonyl groups of DMDDDGA molecules are coordinated to metal ions. The extraction behaviour of DMDDDGA on the Gd(III), Dy(III), Ho(III), Er(III) is positive sequence extraction with the atomic number.

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